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PRELIMINARY TESTS OF SOME CHLOROACETIC ACID ESTERS AS
INSECTICIDES AND MITICIDES

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In the course of screening a number of compounds as insecticides and miticides, several esters of chloroacetic acid showed some activity against selected species. In order to find more effective compounds and also determine any chemical structure relationships to toxicity, a large series of these esters were prepared and tested against five species of arthropods.

The chloroacetates were synthesized by the usual methods. Wherever practical, the acid was esterified with the alcohol by the azeotropic method, using benzene as a solvent and *p*-toluenesulfonic acid as a catalyst. Phenols and difficult-to-esterify hydroxy compounds were esterified in benzene solution with chloroacetyl chloride either with pyridine as an acid acceptor or without pyridine, in which case the mixture was either warmed or refluxed to complete the reaction.

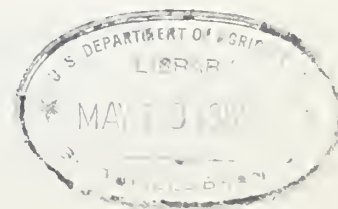
The compounds tested, together with their physical constants, are given in table 1. They are arranged in Chemical Abstracts index form according to their empirical formulas.

The esters were tested against five species, as follows:

Boll weevil (Anthonomus grandis Boh.). One cage containing 20 two- or three-day-old adults was sprayed in the horizontal wind tunnel with 4 cc. of an acetone solution of the test chemical and mortality counts were made 48 hours later.

Cotton aphid (Aphis gossypii Glov.). Cotton seedlings infested with cotton aphids were placed on a turntable in the horizontal wind tunnel, where they were sprayed with 5 cc. of an acetone solution of the test chemical. Mortality counts were made 24 hours later.

Two-spotted spider mite (Tetranychus telarius (L.)). The same method was used as for the cotton aphid. Mortality counts were made 48 hours later.



Salt-marsh caterpillar (Estigmene acrea (Drury)). Each side of a cotton leaf was sprayed in the Potter tower with 5 cc. of an acetone solution of the test chemical. The sprayed leaf was then cut in half and the halves were placed in separate petri dishes, each of which contained 10 fourth-instar larvae. Mortality counts were made 48 hours later.

Southern armyworm (Prodenia eridania (Cram.)). The same method was used as for the salt-marsh caterpillar.

All species except the boll weevil were reared in the laboratory. The boll weevil adults emerged from field-collected squares that had been brought into the laboratory.

There was no appreciable mortality in checks sprayed with acetone only. Pending mortality counts, sprayed insects and mites were held in a constant-temperature room of $80 \pm 2^\circ$ F.; this room was lighted at all times. Mortalities were computed on a straight percentage basis.

The following code is applied in table 2 to indicate the effectiveness and the phytotoxicity of the 98 compounds:

- D - Killed 90% or less at 4%.
- C - Killed 90% or less at 2%.
- B - Killed 90% or less at 1%.
- A - Killed more than 90% at 1%.
- d - Too phytotoxic to count at 4%.
- c - Too phytotoxic to count at 2%.
- b - Too phytotoxic to count at 1%.
- W - Nonphytotoxic at 4%.
- X - Phytotoxic at 4%.
- Y - Phytotoxic at 2%.
- Z - Phytotoxic at 1%.

The cotton seedlings used in the two-spotted spider mite tests were examined in 48 hours for phytotoxicity.

For practical purposes only the highest order of toxicity will be considered--namely, those giving a kill of more than 90% at a concentration of 1% (A). Only three of the esters fell in this class, and only one was toxic to more than one species. The (2-cyclohexyl-4,6-dinitro)-phenyl ester (No. 85) was effective against all the test species except the boll weevil, and the 2-bromoethyl (No. 1) and 1,2-propanediol(di) (No. 9) esters were effective against the southern armyworm.

Summary

Ninety-eight esters of chloroacetic acid, all but one of which were synthesized in the laboratory, were tested against the southern armyworm, salt-marsh caterpillar, boll weevil, two-spotted spider mite, and cotton aphid. Data on phytotoxicity were also obtained. The most toxic compound tested was (2-cyclohexyl-4,6-dinitro)phenyl chloroacetate.

Table 1.--Physical constants and yields of chloroacetic acid esters

Index No.	Ester	Empirical formula	Yield (%)	Boiling point ¹ / (°C./mm. Hg)	²⁵ n _D
1	2-Bromoethyl	C ₄ H ₆ BrClO ₂	98	106/13	1.4880
2	2-Chloroethyl	C ₄ H ₆ Cl ₂ O ₂	77	97/18	1.4610
3	2,3-Dibromopropyl	C ₅ H ₇ Br ₂ ClO ₂	91	104/0.5	1.5330
4	2-Methoxyethyl	C ₅ H ₉ ClO ₃	88	104/20	1.4355
5	Ethylene glycol(di)	C ₆ H ₈ Cl ₂ O ₄	90	106-7/0.4	1.4688
6	Butyl	C ₆ H ₁₁ ClO ₂	--	181-3/760	1.4283
7	Isobutyl	C ₆ H ₁₁ ClO ₂	90	78/26	1.4238
8	(2-Methoxy-1-methyl)- ethyl	C ₆ H ₁₁ ClO ₃	84	90/13	1.4322
9	1,2-Propanediol(di)	C ₇ H ₁₀ Cl ₂ O ₄	79	171/27	1.4625
10	Cyclopentyl	C ₇ H ₁₁ ClO ₂	97	91/10	1.4590
11	1-Ethylpropyl	C ₇ H ₁₃ ClO ₂	87	73/12	1.4298
12	3-Methoxybutyl	C ₇ H ₁₃ ClO ₃	96	106/13	1.4357
13	2-(2-Methoxyethoxy)ethyl	C ₇ H ₁₃ ClO ₄	70	134/12	1.4461
14	Pentachlorophenyl	C ₈ H ₂ Cl ₆ O ₂	27	(131-1.5)	--
15	2,3,4,6-Tetrachlorophenyl	C ₈ H ₃ Cl ₅ O ₂	80	144/1.0	1.5768
16	2,4,5-Trichlorophenyl	C ₈ H ₄ Cl ₄ O ₂	68	(84-5)	--
17	2,4-Dichlorophenyl	C ₈ H ₅ Cl ₃ O ₂	81	(39-40)	--
18	p-Bromophenyl	C ₈ H ₆ BrClO ₂	89	128-30/2.2	1.5615
19	o-Nitrophenyl	C ₈ H ₆ ClNO ₄	82	116/0.8	1.5463
20	p-Nitrophenyl	C ₈ H ₆ ClNO ₄	54	(98-9)	--
21	o-Chlorophenyl	C ₈ H ₆ Cl ₂ O ₂	89	146/14	1.5337
22	p-Chlorophenyl	C ₈ H ₆ Cl ₂ O ₂	80	114-5/1.8	1.5391

Table 1.--Continued

Index No.	Ester	Empirical formula	Yield (%)	Boiling point ¹ / (°C./mm. Hg)	²⁵ n _D
23	Phenyl	C ₈ H ₇ ClO ₂	69	(44-5)	--
24	1,3-Butanediol(di)	C ₈ H ₁₂ Cl ₂ O ₄	93	178/22	1.4627
25	1,4-Butanediol(di)	C ₈ H ₁₂ Cl ₂ O ₄	48	(78-8.5)	--
26	Tetrahydropyran-2-methyl	C ₈ H ₁₃ ClO ₃	81	138-9/14	1.4672
27	Hexyl	C ₈ H ₁₅ ClO ₂	96	104/12	1.4342
28	1,3-Dimethylbutyl	C ₈ H ₁₅ ClO ₂	91	78/12	1.4280
29	2-Methylpentyl	C ₈ H ₁₅ ClO ₂	94	91/12	1.4335
30	2-(2-Ethoxyethoxy)ethyl	C ₈ H ₁₅ ClO ₄	49	138-45/12	1.4474
31	p-Chlorobenzyl	C ₉ H ₈ Cl ₂ O ₂	93	98/0.2	1.5374
32	4-Chloro-o-tolyl	C ₉ H ₈ Cl ₂ O ₂	90	117/1.3	1.5336
33	6-Chloro-o-tolyl	C ₉ H ₈ Cl ₂ O ₂	84	112-3/1.7	1.5300
34	Benzyl	C ₉ H ₉ ClO ₂	92	143/18	1.5243
35	m-Tolyl	C ₉ H ₉ ClO ₂	80	128-9/10	1.5186
36	o-Tolyl	C ₉ H ₉ ClO ₂	86	131-3/14	1.5188
37	p-Tolyl	C ₉ H ₉ ClO ₂	59	128-31/14	1.5250
38	p-Methoxyphenyl	C ₉ H ₉ ClO ₃	92	(49-50)	--
39	Glycerol(tri)	C ₉ H ₁₁ Cl ₃ O ₆	98	176/0.2	1.4838
40	1,5-Pentanediol(di)	C ₉ H ₁₄ Cl ₂ O ₄	98	(60-1)	--
41	4-Methylcyclohexyl	C ₉ H ₁₅ ClO ₂	94	118/17	1.4607
42	Heptyl	C ₉ H ₁₇ ClO ₂	92	119-20/13	1.4372
43	1-Ethylpentyl	C ₉ H ₁₇ ClO ₂	96	100/12	1.4336
44	2,2-Dimethylpentyl	C ₉ H ₁₇ ClO ₂	97	101/12	1.4358
45	Pyrocatechol(di)	C ₁₀ H ₈ Cl ₂ O ₄	85	(56)	--

Table 1.--Continued

Item No.	Ester	Empirical formula	Yield (%)	Boiling point ^{1/} (°C./mm. Hg)	²⁵ n _D
46	Ester with methyl salicylate	C ₁₀ H ₉ ClO ₄	87	136-7/1.2	1.5285
47	Piperonyl	C ₁₀ H ₉ ClO ₄	90	126-7/0.4	1.5440
48	Phenethyl	C ₁₀ H ₁₁ ClO ₂	80	152/18	1.5174
49	<u>m</u> -Ethylphenyl	C ₁₀ H ₁₁ ClO ₂	71	146-8/14	1.5155
50	<u>p</u> -Ethylphenyl	C ₁₀ H ₁₁ ClO ₂	81	150/14	1.5158
51	<u>α</u> -Methylbenzyl	C ₁₀ H ₁₁ ClO ₂	34	172/12	1.5875
52	2-Phenoxyethyl	C ₁₀ H ₁₁ ClO ₃	89	105-6/0.03	1.5235
53	Cyclohexylethyl	C ₁₀ H ₁₇ ClO ₂	98	141/18	1.4680
54	Octyl	C ₁₀ H ₁₉ ClO ₂	97	133-4/13	1.4387
55	1-Methylheptyl	C ₁₀ H ₁₉ ClO ₂	93	110/13	1.4344
56	3-Phenylpropyl	C ₁₁ H ₁₃ ClO ₂	96	168/18	1.5131
57	<u>p</u> -Isopropylphenyl	C ₁₁ H ₁₃ ClO ₂	85	(55.5-6.5)	--
58	(1-Methyl-2-phenoxy)-ethyl	C ₁₁ H ₁₃ ClO ₃	96	139/2.5	1.5122
59	2-Isopropylcyclohexyl	C ₁₁ H ₁₉ ClO ₂	67	134/17	1.4657
60	4-Isopropylcyclohexyl	C ₁₁ H ₁₉ ClO ₂	97	145/18	1.4654
61	Nonyl	C ₁₁ H ₂₁ ClO ₂	93	85-7/0.15	1.4410
62	Ester with 2,6-dimethyl-4-heptanol	C ₁₁ H ₂₁ ClO ₂	94	107/12	1.4341
63	2,4-Dichloro-4-naphthyl	C ₁₂ H ₇ Cl ₃ O ₂	45	(100-1)	--
64	1-Naphthyl	C ₁₂ H ₉ ClO ₂	78	128/0.25	1.6018
65	2-Naphthyl	C ₁₂ H ₉ ClO ₂	53	(95-6)	--
66	6-Bromo- <u>α</u> -(1-bromoethyl)-piperonyl	C ₁₂ H ₁₁ Br ₂ ClO ₄	61	180/0.6	1.5808

Table 1.--Continued

Item No.	Ester	Empirical formula	Yield (%)	Boiling point ¹ / (°C./mm. Hg)	n _D ²⁵
67	(2,6-Dibromo-4- <u>tert</u> -butyl)phenyl	C ₁₂ H ₁₃ Br ₂ ClO ₂	93	(43-4)	--
68	Eugenyl	C ₁₂ H ₁₃ ClO ₃	70	122-3/0.3	1.5311
69	Isoeugenyl	C ₁₂ H ₁₃ ClO ₃	62	(76-7)	--
70	(2-Bromo-4- <u>tert</u> -butyl)-phenyl	C ₁₂ H ₁₄ BrClO ₂	85	119/0.15	1.5352
71	(4- <u>tert</u> -Butyl-2-chloro)-phenyl	C ₁₂ H ₁₄ Cl ₂ O ₂	81	114-6/0.4	1.5221
72	<u>p</u> - <u>tert</u> -Butylphenyl	C ₁₂ H ₁₅ ClO ₂	78	90/0.08	1.5105
73	Carvacryl	C ₁₂ H ₁₅ ClO ₂	90	103/0.05	1.5090
74	2-Ethyl-1,3-hexanediol(di)	C ₁₂ H ₂₀ Cl ₂ O ₄	80	139/1.0	1.4644
75	2- <u>sec</u> -Butylcyclohexyl	C ₁₂ H ₂₁ ClO ₂	33	145/20	1.4670
76	Decyl	C ₁₂ H ₂₃ ClO ₂	99	101-2/0.45	1.4427
77	4- <u>tert</u> -Butyl- <u>m</u> -tolyl	C ₁₃ H ₁₇ ClO ₂	65	102/0.4	1.5129
78	4- <u>tert</u> -Butyl- <u>o</u> -tolyl	C ₁₃ H ₁₇ ClO ₂	73	(47-8)	--
79	Undecyl	C ₁₃ H ₂₅ ClO ₂	83	93/0.25	1.4430
80	(4-Ethyl-1-methyl)octyl	C ₁₃ H ₂₅ ClO ₂	96	150/13	1.4435
81	(2,4-Dichloro-6-phenyl)-phenyl	C ₁₄ H ₉ Cl ₃ O ₂	90	(105-6)	--
82	2-Bromo-4-biphenyllyl	C ₁₄ H ₁₀ BrClO ₂	80	(62-3)	--
83	2-Chloro-4-biphenyllyl	C ₁₄ H ₁₀ Cl ₂ O ₂	62	(53-4)	--
84	<u>p</u> -Biphenyllyl	C ₁₄ H ₁₁ ClO ₂	78	(117-8)	--
85	(2-Cyclohexyl-4,6-dinitro)phenyl	C ₁₄ H ₁₅ ClN ₂ O ₆	52	(79-80)	--
86	<u>o</u> -Cyclohexylphenyl	C ₁₄ H ₁₇ ClO ₂	83	136-8/0.7	1.5314

Table 1.--Continued

Item No.	Ester	Empirical formula	Yield (%)	Boiling point ^{1/} (°C./mm. Hg)	n _D ²⁵
87	<u>p</u> -Cyclohexylphenyl	C ₁₄ H ₁₇ ClO ₂	73	(85-6)	--
88	<u>o</u> -Phenylcyclohexyl	C ₁₄ H ₁₇ ClO ₂	87	116-7/0.25	1.5190
89	6-Pentyl- <u>m</u> -tolyl	C ₁₄ H ₁₉ ClO ₂	81	114/0.5	1.5090
90	2-(<u>p</u> - <u>tert</u> -Butylphenoxy)-ethyl	C ₁₄ H ₁₉ ClO ₃	91	133/0.5	1.5111
91	3-(3-Phenoxypropoxy)-propyl	C ₁₄ H ₁₉ ClO ₄	97	171/2.5	1.4992
92	2-Cyclohexylcyclohexyl	C ₁₄ H ₂₃ ClO ₂	46	105-6/0.25	1.4908
93	2-Butyloctyl	C ₁₄ H ₂₅ ClO ₂	97	162/12	1.4457
94	(2- <u>tert</u> -Butyl-6-isopropyl)phenyl	C ₁₅ H ₂₁ ClO ₂	47	125-6/11	1.5100
95	[2-(<u>p</u> - <u>sec</u> -Butylphenoxy)-1-methyl]ethyl	C ₁₅ H ₂₁ ClO ₃	96	130/0.08	1.5026
96 ^{2/}	<u>p,p</u> -Thiodiphenyl	C ₁₆ H ₁₂ Cl ₂ O ₄ S	--	(123-5)	--
97	<u>p</u> -(<u>a,a</u> -Dimethylbenzyl)-phenyl	C ₁₇ H ₁₇ ClO ₂	90	167-8/0.4	1.5659
98	<u>p</u> -Nonyphenyl	C ₁₇ H ₂₅ ClO ₂	77	143/0.4	1.5048

^{1/} Figures in parentheses are melting points.

^{2/} Sample obtained from Sindar Corp., New York, N. Y.

Table 2.--Biological tests of chloroacetic acid esters

Index No.	ENT No.	Southern armyworm	Salt-marsh caterpillar	Boll weevil	Two-spotted spider mite	Cotton aphid	Phytotoxicity to cotton seedlings
1	22391	A	C	D	D	D	W
2	18412	B	C	D	D	D	W
3	21396	C	C	D	D	D	W
4	18503	D	D	D	D	D	X
5	2151	D	D	D	C	C	Y
6	18528	D	D	D	D	D	W
7	18499	D	D	D	D	D	W
8	22359	D	D	D	D	D	W
9	18500	A	C	D	D	D	W
10	22716	C	D	D	D	D	W
11	18523	D	D	D	D	D	W
12	21925	C	C	D	D	D	W
13	18531	D	D	D	D	D	X
14	19741-A	D	D	D	B	D	Z
15	23376	C	B	D	d	C	Y
16	23267	C	B	D	d	D	Y
17	23259	C	C	D	d	D	Y
18	23258	C	D	D	d	D	Y
19	23268	B	B	D	d	D	Y
20	23373	C	D	D	b	C	Z
21	23255	C	C	D	D	D	W
22	23256	C	C	D	D	D	X
23	23257	D	D	D	d	D	X
24	18487	C	C	D	D	B	W
25	22440	C	D	D	c	B	Y
26	21189	D	D	D	D	D	W
27	30699	D	D	D	D	D	W
28	18524	C	D	D	D	D	W
29	18529	D	D	D	D	D	W
30	18534	C	D	D	d	D	X
31	22389	C	D	D	D	B	W
32	23265	C	D	D	d	B	X
33	23369	C	B	D	D	D	X
34	18343	D	D	D	D	D	W
35	23386	C	D	D	D	D	W
36	23254	C	C	D	D	D	W
37	23253	C	D	D	D	D	W
38	23385	C	D	D	D	D	X
39	30328	C	D	D	B	D	W
40	18495	C	D	D	c	B	Y
41	18484	C	C	D	D	D	W
42	21528	C	C	D	D	D	W
43	18525	C	D	D	D	D	W

Table 2.--Continued

Index No.	ENT No.	Southern armyworm	Salt-marsh caterpillar	Boll weevil	Two-spotted spider mite	Cotton aphid	Phytotoxicity to cotton seedlings
44	30913	D	D	D	D	D	W
45	23378	C	D	D	d	D	X
46	23383	C	D	D	D	C	W
47	31011	C	D	D	d	B	X
48	18405	C	C	D	D	D	W
49	23261	C	D	D	d	C	X
50	23262	C	D	D	d	C	X
51	18530	C	D	D	D	D	W
52	7345	D	D	D	C	C	Y
53	18409	C	C	D	D	D	W
54	30591	D	C	D	d	C	X
55	18522	B	D	D	D	D	W
56	18407	C	C	D	D	C	W
57	23264	D	D	D	d	C	X
58	22399	C	C	D	D	B	W
59	18414	C	C	D	D	D	W
60	18411	C	C	D	D	D	X
61	30589	D	C	D	D	B	W
62	18526	C	D	D	D	D	W
63	23377	C	D	D	D	D	W
64	23260	C	D	D	c	B	Y
65	23263	D	D	D	d	B	X
66	31061	D	D	D	D	D	W
67	23389	D	D	D	D	D	W
68	23370	C	D	D	D	B	W
69	23374	D	D	D	D	D	W
70	23266	D	D	D	D	D	W
71	23366	C	D	D	D	D	X
72	23269	C	C	D	D	D	X
73	23368	C	C	D	D	C	X
74	18498	C	D	D	D	C	W
75	18417	D	C	D	D	D	W
76	30732	D	C	D	D	B	X
77	23270	D	D	D	D	D	X
78	23367	C	D	D	c	D	Y
79	30900	D	C	D	D	B	X
80	22390	C	D	D	D	C	W
81	23375	C	D	D	D	D	W
82	23387	D	D	D	D	D	X
83	23380	D	D	D	d	C	Y
84	16233	D	D	D	D	D	W
85	23382	A	A	B	A	A	Y
86	2800	C	C	D	d	D	X
87	23371	D	D	D	D	D	W

Table 2.--Continued

Index No.	ENT No.	Southern armyworm	Salt-marsh caterpillar	Boll weevil	Two-spotted spider mite	Cotton aphid	Phytotoxicity to cotton seedlings
88	23384	C	D	D	D	b	W
89	23364	D	D	D	d	C	Y
90	18416	D	D	D	D	B	W
91	22355	C	D	D	C	C	W
92	31051	C	D	D	D	D	W
93	18527	C	D	D	D	B	W
94	23372	C	C	D	C	D	W
95	30424	D	D	D	C	B	W
96	17045	D	D	D	D	D	W
97	23379	D	D	D	C	D	W
98	23381	D	D	D	d	C	X

